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Impact of Contaminants From Oil Shale Processing on Forest Ecosystems

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Oil shale mining and processing in northeast Estonia have brought about several ecological problems. The mined oil shale is used as fuel in power stations and in processing plants producing crude oil and about 40 manufactured articles. Pollutants emitted from oil shale processing and chemical plants include SO_2, CO, NO_x, oil shale fly ash, and organic compounds in which aromatic and aliphatic hydrocarbons, phenols, formaldehyde, etc., are represented. Pollution has caused changes in the condition of the forest ecosystem and the chemical character of soil and ground water. The condition of coniferous forest sites was investigated in 1995–1998. Because of the high concentration of alkaline fly ash in the air, the pH of rain water is somewhat elevated (pH = 7.0–7.1) and exceeds the level regarded as normal for rain water. The analysis of the soil samples showed that the concentrations of Ca, Mg and K, which dominate in the solid fraction of the pollutant mixture, are high, being respectively 18, 14, and 4 times as high as the control. The increases in the concentrations of K, Mg, Cu, Pb, and Ni in stemwood reflect increases in the regional oil shale fly ash deposition. Conifers influenced by high levels of air pollution emitted from the oil shale industry are characterized by retarded growth of needles and shoots and radial growth as a result of disturbances in their mineral nutrition and imbalance in their mineral composition.

Keywords Air pollution, alkalinization, Norway spruce, Scots pine.

Introduction

The Estonian field is the largest commercially exploited oil shale deposit in the world, making up about 3.8 billion tons (Veiderma, 1993). Of the mined oil shale, 90% is used as fuel in power plants and 10% is used in processing plants to produce about 40 manufactured articles including crude oil, fuel oil, resin, mastic, and paraffin (Veiderma, 1993).

At present, oil shale mining and processing are the most important industries in Estonia. Over 40 years of oil shale mining and processing in northeast Estonia appear to have brought about several ecological problems. Pollutants emitted from oil shale processing and chemical plants have a multi-component chemical character. They consist of hazardous gaseous components, solid particles, and aerosols. The proportion of alkaline fly ash in the pollutant mixture has changed from year to year, making up 16–30% of the total air pollution. Of the gaseous pollutants, SO_2 makes up 42–56%, CO 8–10%, and NO_x 2% (Liblik and Kundel, 1995). Also, large amounts of organic compounds are emitted in which aromatic and aliphatic hydrocarbons, phenols, formaldehyde, etc., are represented. The impact of air pollutants on the territory of northeast Estonia has changed the condition of

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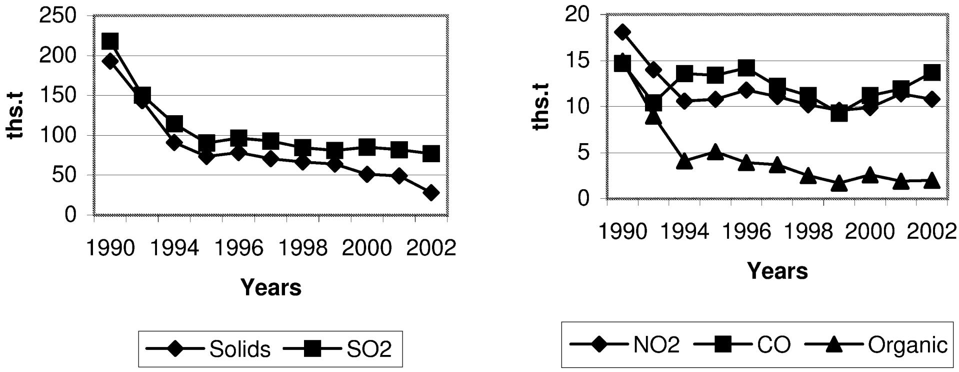

Figure 1. Total emission of pollutants into air in Ida-Viru County (thousand tons per year) (Mandre, 2000).

forest ecosystems (Karoles *et al.*, 1991), bogs (Karofeld, 1996), soils (Kokk, 1991; Petersell *et al.*, 1996), and surface and ground water (Erg *et al.*, 1991).

The northeastern region of Estonia is one of the most heavily forested areas, making up more than 10% of all forested land in Estonia (*Yearbook Forest*, '98, 1998). Forest damage from air pollution, mining and other types of anthropogenic pressure was observed during the period of intensive industrial activity in 1990–1996 (Mandre *et al.*, 1996, 1999). Karoles (1991) showed that crowns of Norway spruces are seriously damaged and the level of defoliation is high in the territories surrounding the main industrial centers.

As a result of the significant reduction of production in recent years, the pollution of the area has also notably decreased (Figure 1). A sharp decline has occurred in the amount and share of solid matter among the air pollutants in the last five years. The proportion of SO_2 in the total emission has increased at present after a decline in 1992–1994. However, a decreasing tendency of amounts of H_2S emitted from Viru Chemistry Group AS was established: 16 t yr^{-1} in 1992 and 8 t yr^{-1} in 1998 (Kundel and Liblik, 1999). No major reduction in the amounts of NO_x and CO was registered.

Considering the disturbances in forest ecosystems in northeast Estonia (Karoles, 1991; Pilt, 1995; Mandre *et al.*, 1996) the objective of the present study was to assess the long-term effects of an air pollutant mixture from the oil shale industry on the forest ecosystem, including the chemical composition of the predominant conifers in Estonian forests (*Pinus sylvestris* L. and *Picea abies* L.). The specific objective of this investigation was to test the hypothesis that biochemical and physiological methods and morphological parameters of the foliage, shoots, and wood of trees can be used for early diagnosis of latent changes caused by alkaline pollution in this region. The condition of coniferous forest sites was investigated in 1995–1998, after a rapid decrease of industrial activity in Kohtla-Järve—the center of oil shale mining and processing.

Study Area and Methods

The study area is situated in northeast Estonia, in Ida-Viru County (Figure 2). Kohtla-Järve, the center of the Estonian oil shale industry, and its surroundings are affected by high amounts of multi-component air pollution and long-term influxes from the local oil shale processing and chemical plant (B), an ammonium and nitrogen fertilizer plant (A), benzoic acid production (C), Kohtla-Järve and other power plants (D, E, F) (Figure 2).

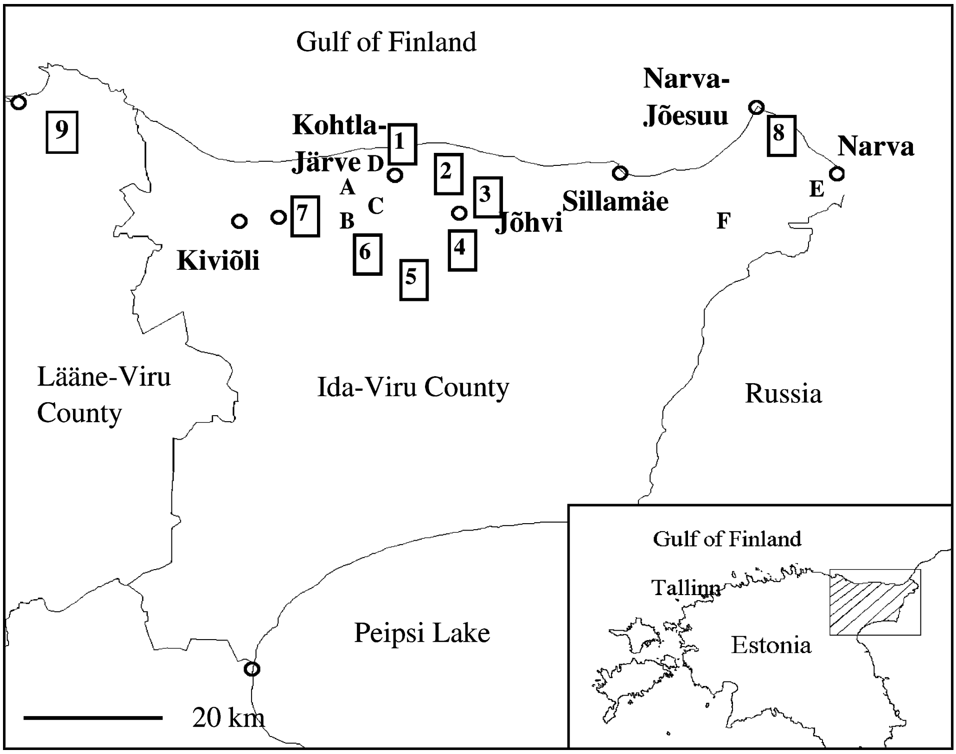

Figure 2. The study area. Location of sample plots (1–8 in squares), control plot (9) and pollution sources: A—Nitrofert AS; B—Viru Chemistry Group AS; C—Velsicol Eesti AS; D—Kohtla-Järve Power Plant; E—Baltic Power Plant; F—Estonian Power Plant.

The climate is transitional from maritime to continental. However, local climatic features in Ida-Viru County are influenced also by large forested areas and numerous mires and bogs (Kaljumäe, 1996). The prevailing winds in coastal areas as well as inland are from south and southwest, the average annual wind velocity ranges from 4.3 to 4.9 m s^{-1}.

Sample plots 1–7 with 60–80-year-old Scots pine and Norway spruce trees were established at different distances and directions from the emission sources in Ida-Viru County (Figure 2, in squares). Sample plot 8 for dendrochemical analyses was established at Narva in the vicinity of the oil shale-fired Baltic Power Plant, the main source of atmospheric pollution in this area. Three control sample plots (9) were located in a relatively unpolluted area in Lahemaa National Park, 78–84 km west of Kohtla-Järve.

Samples of snow, rain, soil, and soil water were collected according to methods described by the International Co-operative Programme on Integrated Monitoring on Air Pollution Effects (Manual for Integrated Monitoring, 1993). The snow samples ($n = 3$) were collected in 1996 from each sample plot (plots 2–7) and from the control area (plot 9) when a permanent winter snow cover had formed. This enabled us to fix the components of precipitation from the beginning of the formation of snow cover to the very moment of sampling. Rain ($n = 16$), soil water ($n = 6$), and soil ($n = 6$) samples were collected during the vegetation period in 1995, 1996, and 1997 from the same sample plots. Cylindrical polyethylene collectors equipped with ash-free paper filters were used to collect rain water (Tuulmets, 1995). The filter restricts solid particles from getting onto the water to be analyzed. Also, the snow melt was filtered before the analysis. Soil samples from the humus horizon for nutrient chemistry were collected with a steel bore cylinder every year in August and September. Soil water was sampled monthly with a lysimeter installed in the soil layer under the humus horizon.

The nutrient status of the upper horizon of soil, soil water, and precipitation was determined in the Laboratory of Soil Chemistry of the Estonian Control Centre of Plant Production, which is accredited by the Estonian Accreditation Centre from 1999 and has competence according to EVS-EN ISO/IEC 17025:2001. Standard methods of soil analysis were used: the content of P and K was determined by the Egner-Riehm double lactate method and that of Ca by Egner-Riehm-Domingo ammonium acetate-lactate method (ISO/11260, 1995). Total N was determined by the Kjeldahl method (ISO/11261, 1995) and the pH of the soil was measured as the potential acidity in H_2O (ISO/10390, 1994). Standard analytical techniques for the characterization of precipitation and soil water chemical composition are described in the Manual for Integrated Monitoring for International Co-operative Programme on Integrated Monitoring on Air Pollution Effects (Manual for Integrated Monitoring, 1993).

For the estimation of changes in conifers, the chemical composition of the samples of one-year-old needles ($n = 12$), shoots ($n = 12$), and stemwood ($n = 28$) from each location were used. Taking into account the results of earlier studies (Kangur, 1988) showing more expressive biochemical response reactions to dust pollution on the more illuminated side of the crown, the samples of one-year-old needles and shoots were taken from the southern side of trees. All the organs of trees were carefully cleaned by removing the foreign substances and by washing the needles with de-ionized water, cut into small pieces and oven-dried at 70°C to stop metabolic activity (Wilde *et al.*, 1979; Landis, 1985). After grinding, 1–2 g of dried plant material of different organs was chemically analyzed in the Laboratory of Plant Chemistry of the Estonian Control Centre of Plant Production. The methods used for analyses are certified by international ringtests including FATAS 2002, AACC, European Grain Network, Estonian/Baltic, etc. Concentrations of metals (Ca, K) were determined using an atom-adsorption analyzer AAA-1N (Karl Zeiss, Jena). Nitrogen was measured by the method of Kjeldahl and P was extracted with vanadium molybdate yellow complex.

For stemwood analysis the sample tree was felled and a 10-cm-wide disk was cut from the stem 1 m above ground in sample plot 8 and in control plot 9. The samples for chemical analysis were taken with a cobalt twist bit from different holes until a sample of the needed weight for each 5-year tree-ring group was obtained. Chemical analyses of the samples were performed in the Central Laboratory of Environmental Research and in the Estonian Control Centre of Plant Production using a Shimadzu atomic absorption/flame emission spectrophotometer (model AA-670). The concentrations of elements (Fe, Cu, Zn, Pb, Ni, Cr and Cd) occurring also in the chemical composition of oil shale fly ash were measured.

Results and Discussion

Precipitation. The precipitation samples collected show significant differences from the control area. The high electric conductivity in both rain water (up to 2.4 times control) and in snow melt (up to 2.6 times control) in the study area indicate a larger amount of dissolved compounds in the precipitation of the industrial region of Kohtla-Järve (Tables 1 and 2). The rain water falling on the ground and vegetation contain large amounts of SO_4^{2-} and elevated concentrations of Ca and K, elements that are present in oil shale fly ash. As the concentration of alkaline fly ash in the air is high, the pH of rain water is somewhat elevated ($pH = 7.0$–7.1) and exceeds the level regarded by Smidt (1984) as normal for rain water

Table 1
Chemical characteristics of rain water in the sample plots (average 1995–1997) (±SE, n = 16)

No. and location of sample plot	Distance, km, and direction of sample plot from emission center	pH	Electric conductivity, mS cm^{-1}	mg l^{-1}				
				Ca^{2+}	Mg^{2+}	K^{+}	SO_4^{2-}	NO_3^{-}
1 Saka	3N	7.1 ± 0.4	0.157 ± 0.012	23.5 ± 2.01	3.0 ± 1.11	18.5 ± 0.92	14.6 ± 0.97	1.2 ± 0.080
2 Kohtla-Järve	0.5NE	7.0 ± 0.6	0.132 ± 0.011	18.8 ± 0.96	1.9 ± 0.94	5.8 ± 0.12	14.2 ± 1.00	1.4 ± 0.043
3 Kukruse	7E	7.1 ± 0.8	0.232 ± 0.021	29.9 ± 2.61	1.9 ± 0.07	9.0 ± 0.09	16.1 ± 1.42	1.9 ± 0.060
6 Sompa	6S	7.1 ± 0.2	0.143 ± 0.016	20.3 ± 1.12	1.7 ± 0.01	11.0 ± 0.01	15.2 ± 0.95	1.6 ± 0.011
9 Lahemaa (control)	81W	6.6 ± 0.3	0.091 ± 0.001	9.3 ± 0.41	1.4 ± 0.06	2.0 ± 0.07	4.9 ± 0.16	0.7 ± 0.001

Table 2

Chemical characteristics of snow melt at different distances from Kohtla-Järve in 1996 (n = 3)

No. and location of sample plot	Distance, km, and direction of sample plot from Kohtla-Järve	pH	Electric conductivity, mS cm^{-1}	mg l^{-1}						
				Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	NO_3^-	SO_4^{2-}
2 Kohtla-Järve	0.5NE	8.3	47.2	8.2	0.36	0.30	0.6	0.35	0.56	7.1
3 Kukruse	7E	8.6	58.9	9.2	0.40	0.20	2.4	0.25	0.56	7.4
5 Kalina	14S	7.3	43.7	6.3	0.52	0.30	0.5	0.21	0.43	9.3
6 Sompa	6S	7.4	47.7	8.9	0.43	0.20	0.5	0.27	0.48	7.8
7 Aa	6W	8.7	40.1	13.7	0.25	0.30	0.3	0.12	0.50	4.2
9 Lahemaa (control)	81W	6.8	22.5	4.3	0.14	0.15	0.6	0.17	0.30	2.4

(pH = 5.1–6.1). Differences between the mean pH on sample plots and the control plot were statistically significant on the level $p < 0.05$.

The analysis of the snow samples collected in 1996 showed that the pH of snow melt was 7.3–8.7 in the sample plot area and 6.8 in the control plots, and the differences between mean pH on the sample plots (2–7) in Kohtla-Järve area and the control plot (9) were significant ($p = 0.001$). The concentrations of the elements dominating in the pollutant mixture (Ca, Mg, K, S, N) were also significantly (for Ca, K, and N $p < 0.05$ and for Mg and S $p < 0.001$) higher in the snow collected in the Kohtla-Järve area than in the control samples from Lahemaa (Table 2).

Soil. Pollutants from the oil shale industry reach the soil surface via dry and wet deposition and change the chemical and physical properties of upper horizons of the soil, especially of the litter and humus horizons. Alkalinization of soils is clearly observed (Table 3). This phenomenon was also described by Kokk (1991) in mapping forest soils in this region.

The analysis of the soil samples taken from the humus horizon in 1996 and 1997 showed that in the Kohtla-Järve area the concentrations of Ca, Mg and K, are respectively 10, 6 and 3 times as high as the control (Table 3). Large differences ($p < 0.05$) from the control were observed in the total S content in soil (up to 4 times as high as the control). In 1986–1990 the mean N content in humus horizons of soils in the Kohtla-Järve region was several times higher than in the soils of the same type at Lahemaa (0.4 mg 100 g^{-1}) (Mandre *et al.*, 1996) being 1.9 mg 100 g^{-1} at a distance of 0.5 km NE (sample plot 2), 2.57 at 2 km W and 1.58 at the 3 km N from Kohtla-Järve (sample plot 1). Studies in 1997 suggested a decreasing tendency of N in humus horizons compared to previous years. High values of electric conductivity of soil solutions indicate a strong pollution of soil in the study area.

Soil Water. The analysis of the soil water samples collected from the study plots under the humus horizon reflected those of the soil samples in terms of the chemical composition and electric conductivity (Table 4). The pH of soil water was especially high in the sample plot 4 in the vicinity of the Ahtme power plant, where an elevated electric conductivity and higher amounts of Ca were found in soil water. The mean content of Mg and S varied in different sample plots being somewhat higher (plots 4, 5, 6, 7) or unchanged (plots 2 and 3) compared to the unpolluted control. The content of Fe and Mn in the soil water of the studied area was significantly ($p < 0.05$) lower than the control due to their reduced solubility in an alkaline medium (Table 4).

Chemical Composition of Trees. Conifers exposed to high levels of air pollution emitted from the oil shale industry are characterized by retarded growth of needles and shoots and radial growth as a result of disturbances in their mineral nutrition and imbalance in their mineral composition (Mandre *et al.*, 1999; Ots *et al.*, 2000). Foliar, shoot and stemwood analyses provide a means for detecting changes in the content of nutrients and contaminants allowing for assessment of element fluxes and nutritional status of forest trees or are an effective means of recognizing emission-related stress in trees.

Although the level of air pollution emitted from Kohtla-Järve industrial enterprises has decreased considerably (Figure 1), the foliar diagnosis of the accumulation of pollution components still demonstrated differences between the trees in the industrial territory and in the unpolluted control area. It has been found that plants easily assimilate Ca and K from the growth substrate with pH over 6.5 (Marschner, 1986). About 15% higher average content of Ca was found in one-year-old needles and 23% higher content in shoots of Norway spruce if compared to the control, while the average content of K was not substantially

Table 3

Chemical characteristics of the humus horizon in the sample plots in 1996–1997 (±SE, n = 6)

No. and location of sample plot	Distance, km, and direction of sample plot from Kohtla-Järve	pH	Electric conductivity, mS cm^{-1}	mg $100g^{-1}$					
				S	(Available to plants)				
				(Total)	Ca	Mg	K	P	Fe
2 Kohtla-Järve	0.5NE	6.8 ± 0.1	1.09 ± 0.06	55 ± 5.2	659 ± 163	29.3 ± 1.5	8.9 ± 3.06	1.32 ± 0.06	2.00 ± 0.21
3 Kukruse	7E	5.8 ± 1.0	0.78 ± 0.35	60 ± 4.4	484 ± 55	40.0 ± 43.3	11.0 ± 4.9	0.40 ± 0.01	3.3 ± 0.09
4 Kose	15SE	7.4 ± 0.1	1.47 ± 0.15	80 ± 5.3	1533 ± 275	127.6 ± 22.5	15.2 ± 1.5	1.01 ± 0.10	5.3 ± 0.98
5 Kalina	14S	5.8 ± 0.5	1.59 ± 0.17	165 ± 18.1	983 ± 238	60.6 ± 1.1	17.9 ± 5.8	1.19 ± 0.10	5.7 ± 1.41
6 Sompa	6S	4.7 ± 0.1	0.59 ± 0.03	50 ± 1.9	173 ± 35	13.0 ± 4.3	4.3 ± 0.3	0.66 ± 0.09	8.6 ± 2.11
7 Aa	6W	5.9 ± 0.9	1.52 ± 0.36	135 ± 10.2	1258 ± 181	73.7 ± 26.8	14.7 ± 3.2	1.01 ± 0.10	5.5 ± 0.12
8 Narva-J oesuu	25E	6.3	2.16	50	70	64	16	2.1	28.5
9 Lahemaa (control)	81W	3.6 ± 0.3	0.48 ± 0.03	43 ± 8.9	85 ± 38	9.2 ± 3.9	4.7 ± 2.0	1.85 ± 0.14	0.6 ± 0.01

Table 4
Chemical characteristics of soil water in the sample plots in 1996–1997 (±SE, n = 6)

No. and location of sample plot	Distance, km, and direction of sample plot from Kohtla-Järve	pH	Electric conductivity, mS cm^{-1}	mg $100g^{-1}$					
				Ca^{2+}	Mg^{2+}	K^{+}	Mn^{2+}	Fe^{3+}	SO_4^{2-}
2 Kohtla-Järve	0.5NE	6.9 ± 0.4	0.12 ± 0.01	19.0 ± 3.3	2.2 ± 1.5	7.0 ± 0.2	0.005 ± 0.002	0.081 ± 0.04	10.6 ± 8.3
3 Kukruse	7E	6.4 ± 0.3	0.07 ± 0.02	9.6 ± 2.1	1.3 ± 0.6	1.8 ± 0.8	0.009 ± 0.004	0.182 ± 0.129	8.4 ± 3.7
4 Kose	15SE	7.2 ± 0.5	0.21 ± 0.03	46.6 ± 7.8	3.1 ± 0.3	4.4 ± 2.3	0.018 ± 0.011	0.110 ± 0.024	18.7 ± 6.7
5 Kalina	14S	6.4 ± 0.4	0.16 ± 0.07	26.9 ± 7.9	3.7 ± 1.6	7.5 ± 3.2	0.005 ± 0.001	0.266 ± 0.076	13.3 ± 6.4
6 Sompa	6S	6.1 ± 0.7	0.22 ± 013	17.1 ± 4.7	4.1 ± 0.4	24.4 ± 8.7	0.032 ± 0.002	0.294 ± 0.021	36.7 ± 26.6
7 Aa	6W	5.9 ± 0.4	0.21 ± 0.11	28.2 ± 13.4	4.0 ± 2.1	9.5 ± 2.2	0.010 ± 0.005	0.269 ± 0.094	16.5 ± 8.4
9 Lahemaa (control)	81W	5.1 ± 0.3	0.08 ± 0.01	11.4 ± 3.3	1.8 ± 0.5	4.6 ± 1.0	0.041 ± 0.011	0.882 ± 0.194	9.5 ± 5.2

different from the control and the content of Mg in the needles was even somewhat lower than that in the control (Table 5). Statistically significant differences (t-test) from the control in average content of elements in Kohtla-Järve area were established only for Ca in needles ($p = 0.0034$) and in shoots ($p = 0.002$). Disproportionality of the accumulation of these macronutrients by plants was earlier ascertained in alkaline growth conditions in the vicinity of a cement plant (Mandre, 1995), which can be explained as antagonistic effects reflecting competition of different cations for soil exchange sites or maintenance of charge balance in the plant (Marschner, 1986; Timmer, 1991). However, the earlier investigations (Pärn, 2000) demonstrated that in the stemwood of Scots pine under the influence of oil shale fly ash (plot 8) the concentrations of K and Mg were higher and the concentrations of Ca lower than in the stemwood of pines in the control sample plot. Regression analysis of the content of different elements in Norway spruce needles and soil pH in the humus horizon showed that soil pH could be responding to the accumulation of Ca^{2+} ($R^2 = 0.617$), K^+ ($R^2 = 0.568$) and Mg^{2+} ($R^2 = 0.528$) in needles.

The availability of several metals may be inhibited by alkalinization of soil (Marschner, 1986). In our studies the content of Cu and Zn in Norway spruce as a mean in the different sample plots of oil shale processing region has decreased respectively by 28% and 29% in the needles and 15% and 4% in the shoots compared to the control trees (Table 5). The assimilation of Fe into the needles and shoots of Norway spruce showed an essential increase (Table 5). The reasons for increased Fe in needles and shoots of Norway spruce in alkaline areas need further research. It seems that the pH of soil between 6.8 and 7.4 and soil water from 5.9 to 7.2 is not limiting Fe nutrition in industrial areas or the increase of Fe in compartments of trees. Mashhady and Rowell (1978) showed that in alkaline soil (pH > 7) with high organic matter the solubility of Fe is governed not by inorganic Fe forms but by the formation of chelated Fe, obtainable by plants. As phenolics and organic acids, occurring in the air pollutant mixture emitted from oil shale processing and accumulating in soils affected (Liblik and Rätsep, 1994; Liblik and Kundel, 1995; Kundel and Liblik, 1999), have been identified as major Fe chelating compounds (Marschner, 1986), the increase of Fe in trees in the Kohtla-Järve area may be due to Fe chelation.

The contents of Fe, Cd and Zn in the stemwood of Scots pine (plot 8) were essentially lower than in the control trees (Table 6). The mean concentrations of Pb, Cu, and Ni were higher than that in the control plot but differences were statistically insignificant.

Regression analysis showed a linear relationship between the soil water pH and the concentration of Fe^{3+} ($R^2 = 0.671$), Cu^+ ($R^2 = 0.656$) and Mn^{2+} ($R^2 = 0.512$) in needles. It was shown earlier that Mn deficit has developed in spruces and pines in the areas surrounding the cement plant in Kunda (Estonia) at soil pH 6.7–8.1, snow melt pH 10–12 and rain pH 7.6–8.1 (Annuka and Mandre, 1995; Tuulmets, 1995; Mandre, 2000). Similar results have been obtained in the oil shale processing area, where the average Mn concentration in the needles and shoots of Norway spruce was respectively only 19% and 30% of the control and twofold lower in the stemwood of Scots pine in the sample plot 8. The essential decrease of Mn in trees is explained by alkalinization of the environment in which Mn^{2+} compounds turn into Mn^{3+} or Mn^{4+} compounds, having a low solubility, and are practically not available to plants (Marschner, 1986). Also, the availability of Cu and Zn at alkaline pH of soils is decreased due to co-precipitation with Ca carbonates and phosphates (Krause, 1991) explaining the decrease of these metals in the needles and shoots of trees in the area influenced by air pollution from oil shale processing.

High levels of SO_2 in air pollution complex and the environment (Figure 1, Tables 1, 2, 3 and 4) have led to increasing S concentrations in spruce needles, which make up

Table 5

Content of nutrients in one-year-old needles and shoots of Norway spruce (±SE, n = 12)

No. and location of sample plot	Total content of mineral elements (% dw)	N (% dw)	S (% dw)	P ($g\ kg^{-1}$)	K ($g\ kg^{-1}$)	Ca ($g\ kg^{-1}$)	Mg ($g\ kg^{-1}$)	Fe ($mg\ kg^{-1}$)	Mn ($mg\ kg^{-1}$)	Zn ($mg\ kg^{-1}$)	Cu ($mg\ kg^{-1}$)
Needles											
2 Kohtla-Järve	4.06 ± 0.9	1.17 ± 0.13	0.152 ± 0.006	1.27 ± 0.02	10.9 ± 1.2	8.7 ± 0.04	2.10 ± 0.21	60.0 ± 2.1	11.7 ± 0.9	36.1 ± 3.1	24.9 ± 2.1
3 Kukruse	3.50 ± 0.8	1.03 ± 0.13	0.092 ± 0.001	1.46 ± 0.02	10.7 ± 1.7	6.9 ± 0.20	2.08 ± 0.31	48.0 ± 1.9	164.5 ± 8.2	35.0 ± 2.4	35.0 ± 2.7
4 Kose	3.64 ± 0.8	0.99 ± 0.09	0.095 ± 0.003	1.56 ± 0.04	10.8 ± 0.8	7.5 ± 0.68	1.95 ± 0.09	52.6 ± 3.4	114.0 ± 3.4	28.5 ± 2.4	28.5 ± 2.2
5 Kalina	3.50 ± 0.1	1.02 ± 0.11	0.167 ± 0.008	1.09 ± 0.02	9.8 ± 0.9	7.5 ± 0.61	2.24 ± 0.18	39.3 ± 3.1	48.8 ± 3.1	22.5 ± 2.1	22.5 ± 2.4
6 Sompa	3.82 ± 0.2	1.18 ± 0.17	0.086 ± 0.012	1.27 ± 0.03	12.4 ± 1.2	7.3 ± 0.79	2.05 ± 0.18	45.0 ± 2.8	65.9 ± 4.1	24.9 ± 3.0	36.6 ± 1.9
7 Aa	4.68 ± 0.2	1.17 ± 0.02	0.102 ± 0.013	1.37 ± 0.06	12.6 ± 1.3	7.9 ± 0.26	2.49 ± 0.17	49.0 ± 4.2	61.2 ± 4.4	18.5 ± 1.9	20.0 ± 1.0
9 Lahemaa (control)	3.53 ± 0.3	0.94 ± 0.18	0.080 ± 0.002	1.43 ± 0.05	10.5 ± 0.9	6.6 ± 0.37	2.85 ± 0.21	29.9 ± 3.0	420.0 ± 8.7	38.6 ± 1.9	38.6 ± 1.7
Shoots											
2 Kohtla-Järve	2.73 ± 0.08	0.94 ± 0.01	0.047 ± 0.007	1.3 ± 0.21	10.0 ± 1.1	6.6 ± 0.02	1.52 ± 0.03	131 ± 12.1	124 ± 6.8	61.8 ± 8.9	8.76 ± 0.9
3 Kukruse	2.98 ± 0.12	0.84 ± 0.01	0.045 ± 0.004	1.3 ± 0.09	10.4 ± 1.0	6.3 ± 0.02	1.95 ± 0.1	126 ± 9.3	125 ± 7.1	54.5 ± 2.6	7.63 ± 1.9
4 Kose	3.34 ± 0.11	0.67 ± 0.01	0.046 ± 0.006	1.32 ± 0.08	11.2 ± 0.9	6.3 ± 0.08	1.46 ± 0.09	302 ± 3.9	57.8 ± 3.4	51.0 ± 2.2	6.6 ± 2.1
5 Kalina	2.86 ± 0.09	0.82 ± 0.03	0.043 ± 0.004	1.06 ± 0.1	9.7 ± 0.9	6.6 ± 0.07	1.46 ± 0.06	139 ± 5.6	32 ± 3.1	45.9 ± 1.9	7.66 ± 0.8
6 Sompa	2.69 ± 0.08	0.89 ± 0.04	0.044 ± 0.008	1.24 ± 0.1	10.5 ± 0.8	6.0 ± 0.06	1.74 ± 0.12	123 ± 11.1	42.4 ± 2.9	50.9 ± 1.9	7.32 ± 0.9
7 Aa	2.73 ± 0.12	0.95 ± 0.04	0.042 ± 0.007	1.25 ± 0.08	10.7 ± 1.1	6.0 ± 0.02	1.82 ± 0.1	130 ± 10.1	37.2 ± 5.1	33.6 ± 2.6	6.96 ± 1.1
9 Lahemaa (control)	2.49 ± 0.15	0.66 ± 0.03	0.039 ± 0.004	1.13 ± 0.07	10.1 ± 0.6	5.1 ± 0.01	1.49 ± 0.1	76 ± 6.8	222 ± 10.6	51.6 ± 2.1	8.8 ± 0.6

Table 6

Content of elements in stemwood samples of Scots pine and the statistical significance (p) of the differences from the control (t-test) (±SE, n = 28)

No. and location of sample plot	mg kg^{-1}						
	Fe	Zn	Cr	Cd	Pb	Cu	Ni
8 Narva	3.86 ± 0.23	5.95 ± 0.18	0.20 ± 0.01	0.17 ± 0.01	0.56 ± 0.05	2.34 ± 0.05	0.64 ± 0.04
9 Lahemaa (control)	4.84 ± 0.23	7.89 ± 0.52	0.21 ± 0.03	0.31 ± 0.03	0.37 ± 0.04	2.09 ± 0.05	0.58 ± 0.05
p	0.01	0.001	ns	0.05	ns	ns	ns

about 45% of the S content in the control trees (Table 5). Regression analysis showed a linear relationship between the S concentrations in needles and the SO_4^{2-} content in soil ($R^2 = 0.564$), soil water ($R^2 = 0.697$), and also with the electric conductivity of soil water ($R^2 = 0.608$). The increase in the S content in shoots was calculated at 14% of the control.

The highest S concentrations in Norway spruce needles and shoots were established in sample plots 1 and 2, located leeward from the prevailing winds from the towns of Kiviõli and Kohtla-Järve. In sample plot 2 the S content in the needles and shoots was respectively 90% and 21% higher than in the unpolluted territory.

In sample plot 5, which is affected by Ahtme power plant and an oil-shale enrichment plant, the S content in needles was twice as high as in the control samples. The accumulation of SO_4^{2-} is intensified by alkaline growth conditions as shown by Marschner (1986) and Klemm (1989).

Other dominating pollutants in this region, NO_x and NH_3, have been essentially affecting the nitrogen cycle in the forest ecosystem. It is possible that trees actively obtained N compounds not only from the soil, but also from the air and precipitation, resulting in a very high N level in plant tissues (Mandre *et al.*, 1996). Analyses in 1997 indicated 3–12% higher content of the NO_3-N in the humus horizon of the soil in the polluted area than in the control. Regression analyses revealed a relationship between N in soil and needles ($R^2 = 0.516$) and shoots ($R^2 = 0.618$), but not between the content of N compounds in needles and in precipitation ($R^2_{N/NO_3^-} = 0.475$; $R^2_{N/NH_4^+} = 0.111$).

The results of the dendrochemical analysis of the Scots pine stemwood in sample plot 8 suggest a strong relationship between the time trends of concentrations of P, K, Zn, Cu, and Cr and the amount of oil shale fly ash emitted by the Baltic Power Plant, but not between the radial growth of pines in this sample plot and oil shale fly ash emissions of directly preceding years (Pärn, 2001, 2002). A positive relationship between the radial growth of trees and the emitted amounts of oil shale fly ash was detected when emissions older than 5 years were compared with the present growth.

Conclusions

Prolonged effect of the multi-component air pollution from oil shale processing and production in Northeast Estonia has substantially affected biogeochemical cycling in forest ecosystems. The comparatively high concentrations of alkaline ash (pH > 12) and various gaseous pollutants (organic and inorganic) in the atmosphere of the investigated areas over 40 years have caused quantitative and qualitative changes in the chemical character of precipitation, forest soil and soil water. Although the levels of air pollutants emitted by the industry have seriously decreased in recent years, alkaline reaction of the growth environment of trees is still essential in some regions. In the territory surrounding the center of oil shale processing the average pH of rainwater, snow melt, soil humus horizon and soil water had increased due to relatively high concentrations Ca, K and Mg in oil shale ash emitted from the industry and due to accumulation of these elements in the environment.

The foliar diagnosis of the accumulation of pollution components still demonstrated differences between the trees in the industrial territory and in the unpolluted control area. Alkalinization of soils and soil water in the sample plots complicated mineral nutrition processes and disbalanced mineral elements composition in trees. A relatively high average content of Ca was found in one-year-old needles and shoots if compared to the control, while the average content of K was not substantially different from the control, and the content of Mg in the needles was even lower than that in the control. Regression analysis showed that soil pH could be responding to the accumulation of Ca, K and Mg in needles.

The decrease of Mn, Cu, and Zn in the needles and shoots of trees in the area influenced by air pollution from oil shale processing indicates the decreased availability of these metals to plants at alkaline pH of soils. Increased S and N in the plant tissues are a direct consequence of elevated concentrations of N and S compounds in the air due to pollution affecting the plant directly through the leaf cuticle or through the soil.

The results of the dendrochemical analysis of the Scots pine stemwood suggest a strong relationship between the time trends of concentrations of P, K, Zn, Cu, and Cr and the amount of emitted oil shale fly ash. A positive relationship between the radial growth of trees and the emitted amounts of oil shale fly ash was detected when emissions older than 5 years were compared with the present growth.

Changes in abiotic components of forest ecosystem may be a risk for the development and bioproduction of trees. Obviously the composition of the needles and shoots of conifers is affected in addition to the current air pollution also by pollutants accumulated in the soil during previous years.

The ecophysiological studies allowed us to find biochemical parameters suitable for assessing the state of trees and its changes. The use of biochemical methods will be an essential complementing for forest monitoring system. In dust-affected areas estimation of the vitality of trees with the help of morphological parameters and assessment of the long-term changes in the whole ecosystem are possible.

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